DELOCALIZATION AND STABILITY OF *o*-AND *p*-QUINONE METHIDES: A HMO STUDY*

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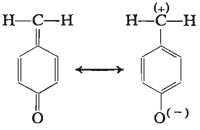
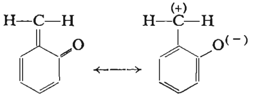
A series of twenty one *p*- and *o*-quinone methides has been investigated by the HMO method. Stability predictions for compounds *I—XIII* are based on a combination of their topological resonance energy, nucleophilic reactivity and dimerization ability. The obtained results have been verified by the synthesis of four new quinone methides *IIb*, *Vb*, *VIa* and *VIb*.

The increased interest in the chemistry of quinone methides observed in the last years has been initiated mainly by the fact that these compounds participate in the biosynthesis and degradation of lignin[1,2] and in some other biochemical processes[3,4]. The simplest quinone methides *Ia* and *IIa* are of interest also from the theoretical point of view because they are in an intermediary position between the π-isoelectronic quinodimethanes and quinones. However, unlike in quinones and quinodimethanes, the arrangement of π-orbitals in quinone methides corresponds to a higher resonance energy than in a comparable acyclic structure. The well-known ability of quinone methides to react in "aromatic", charge separated forms may be considered as a manifestation of this fact.



Ia



IIa

Both the parent quinone methides *Ia* and *IIa* are undoubtedly highly reactive compounds because they have been hitherto detected only in a matrix at very low temperatures[5] or in dilute solutions by means of spectroscopy[6]. On the other hand, it is known that replacement of methylene hydrogens by suitable substituents (phenyl

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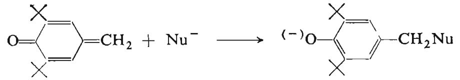
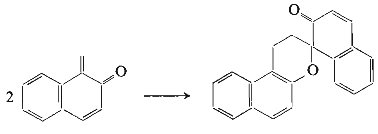
groups[7]) or annelation of aromatic rings to the parent system[8] leads in the *para*-series to stable, crystalline compounds. It is therefore obvious that the stability of quinone methides strongly depends on their structure, *i.e.* is generally a function of conjugation and of the electronic (and in some cases also steric) effect of substituents. Theoretical studies of the formally similar annulenones have shown[9] that their stability depends on the following three independent factors: *a*) aromatic stability due to cyclization and conjugation, *b*) kinetic stability (reactivity) of the exocyclic double bonds, and *c*) strain energy. For quinone methides, the strain energy is negligible (formation of the six-membered quinonoid cycle) and therefore their stability is determined by the contributions *a*) and *b*).

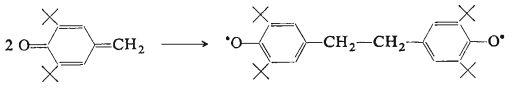
The problem of aromatic stabilization has recently been treated in several reviews[10-13] and several methods have been suggested for the quantitative description of aromaticity. One of the most widely used approaches is the modified[14,15] HMO calculation of resonance energy using parameters based exclusively on properties of molecules in the ground electronic state and on a suitably chosen reference system. If we define the resonance energy per electron (REPE) as a difference between Hückel π-energy and π-energy of the "localized" structure, divided by the number of π-electrons, then this quantity must correlate with thermodynamic stability. This approach has been successfully used in calculation of aromatic stabilization in 4n π-electron annulenones[15] and quinodimethanes[16]. The aromatic stabilization in quinone methides has not hitherto been studied. As far as kinetic stability of quinone methides is concerned, its manifestation is the ability to add nucleophiles[17] to the methide carbon (*A*) and/or to undergo dimerization[18,19] (*B*), (*C*)



(*A*)



(*B*)



(*C*)

Within the framework of systematic study of quinone methides we performed HMO calculation of the REPE values and reactivity indexes for 21 compounds described by the formulae *I*–*XIII*. The aim of our work was *1*) to determine the extent of participation of aromatic stabilization to the total stability of quinone methides as a function of structure, 2) to predict the relative order of stability of quinone methides and to confirm it experimentally by synthesis of hitherto not described compounds.

EXPERIMENTAL

Electronic spectra were taken in dichloromethane on a Specord UV-VIS (Zeiss, Jena) instrument (scanning speed 16·7 $\text{cm}^{-1}\,\text{s}^{-1}$), IR spectra were recorded on a Perkin–Elmer 621 spectrophotometer (0·1 mm cell) in tetrachloromethane.

Quinone methides *IIb*, *Vb*, *VIa* and *VIb* were prepared from the corresponding alcohols by the described procedure[6] and their spectral properties are given in Table I. The alcohols were synthesized as described previously[20–22] and their physical constants were in accord with the published values.

The π-electronic energies of all the 21 compounds studied were obtained by the HMO procedure using recommended[15] parameters for the oxygen atom ($h_O = 0{\cdot}22$, $k_{C=O} = 0{\cdot}99$). In this parameterization the maximum statistical weight is ascribed to the quinonoid and charge separated structures whereas minimum weight is ascribed to the biradical form which concerns predominantly the excited state. For fuchsones, the resonance energy calculations included also geometry of the phenyl groups, as determined by structural analysis of 2,6-dibromofuchsone[23] and 1-diphenylmethylene-1,2-naphthoquinone[24]. On the basis of this analysis we suggested two approximative models, one for *p*-fuchsones with the resonance integral $\beta_{C-C_6H_5} = 0{\cdot}95\beta_{C=C}$, the second for *o*-fuchsones with $\beta_{C-C_6H_5} = 0{\cdot}85\beta_{C=C}$.

The Klopman reactivity index[25] was calculated in the approximation of a single-orbital reagent with energies $\varepsilon_{Nu} = 0{\cdot}3\beta$, $0{\cdot}2\beta$, $0{\cdot}1\beta$, 0 and $-0{\cdot}1\beta$. The limit value of $+0{\cdot}3\beta$ represents a "hard" nucleophilic reagent whereas the value $-0{\cdot}1\beta$ concerns a ' soft" reagent. Dimerization ability of quinone methides was evaluated within the framework of the general perturbation theory by the magnitude of overlap stabilization between pairs of various interacting centers. The numerical calculation was carried out using the published relationship[26], the dimerization of *o*-quinone methides (*B*) being treated as non-synchronous cycloaddition.

RESULTS AND DISCUSSION

The fact that all the REPE values calculated for derivatives *I–XIII* are positive (Table II) and range between 0·0255β and 0·0539β indicates that in quinone methides electron delocalization plays an important role. The REPE values for the parent quinone methides *Ia* and *IIa* are comparable with those for cyclopropenone[15] (0·032β) to which a significant aromatic character is ascribed. REPE values of other compounds exhibit structural dependences. Annelation of benzenoid units to the parent structure has a strongly stabilizing effect. This is particularly marked in case of compounds *XI* and *XII* (REPE = 0·0539β) in which both endocyclic double bonds of the parent compound are incorporated in the aromatic ring. This finding agrees well with some accepted criteria of aromaticity[27] such as that for $4n$ π-electron molecules the aromaticity index must increase with increasing number of π-electrons (unlike for the $4n + 2$ π-systems). The increase in aromatic stabilization due to annelation in quinone methides (QM) can be, in the first approximation, correlated with that in quinodimethanes (QDM) and quinones (Q) (refs[16,28], although correlations of the type $\mathrm{REPE}_{\mathrm{Q}} = A.\ \mathrm{REPE}_{\mathrm{QD}} + B$ (or $\mathrm{REPE}_{\mathrm{QDM}} = A.\ \mathrm{REPE}_{\mathrm{QM}} + B$)

TABLE I
Spectral Characteristics of Quinone Methides

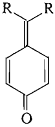
Compound	*IIb*	*Vb*	*VIa*	*VIb*
$\nu_{\max}$, nm	424·0	487·5	395·5	383·0
$\tilde{\nu}$(C=O), cm^{-1}	—	1 617·0	—	1 635·0

TABLE II
Calculated Resonance Energies of Some Quinone Methides

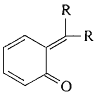
Compound	n^a	Additive $E[\beta]$	HMO $E[\beta]$	RE[β]	REPE[β]^b
Ia	8	9·8811	10·1532	0·2721	0·0340
Ib	20	26·1569	27·0406	0·8837	0·0442
IIa	8	9·9105	10·1811	0·2706	0·0338
IIb	20	26·1863	26·8986	0·7123	0·0356
IIIa	12	15·4602	16·0268	0·5666	0·0472
IIIb	24	31·7360	32·7191	0·9831	0·0410
IVa	12	15·4602	16·0248	0·5646	0·0470
IVb	24	31·7360	32·7296	0·9936	0·0414
Va	12	15·4059	15·7114	0·3055	0·0255
Vb	24	31·6817	32·6298	0·9481	0·0395
VIa	12	15·4353	15·7644	0·3291	0·0274
VIb	24	31·7111	32·5004	0·7893	0·0329
VIIa	12	15·4602	16·0248	0·5646	0·0470
VIIb	24	31·7360	32·8887	1·1527	0·0480
VIII	12	15·4647	15·7966	0·3319	0·0277
IX	12	15·4353	15·7606	0·3253	0·0271
X	12	15·4353	15·7559	0·3206	0·0267
XIa	16	21·0393	21·9009	0·8616	0·0539
XIb	28	37·3151	38·7422	1·4271	0·0510
XII	16	21·0393	21·9009	0·8616	0·0539
XIII	14	17·9373	18·3638	0·4265	0·0305

[a] Number of π-electrons; [b] resonance energy per electron.

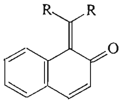
do not hold in general (Fig. 1). Replacement of both hydrogen atoms on the methide carbon by phenyl groups leads to steric repulsions causing a rotation of the benzene rings from the trigonal plane (about 34° in the *para* series and 57° and 75° in the *ortho* series[24]). Therefore, the additive contribution of resonance energy of the two phenyl groups varies considerably. From the relationship[29] $E_{\mathrm{res}} = \mathrm{const} . \cos^2 \varphi$ we can estimate that for *ortho* derivatives it should amount to about 10–20% of the original value so that the phenyl groups behave as weak electron acceptors because of their inductive effect. The low stabilization effect of phenyl groups in the *ortho* series ($\mathrm{REPE}_{\mathrm{IIb}} = 0{\cdot}0358\beta$) relative to that in the *para* series ($\mathrm{REPE}_{\mathrm{Ib}} = 0{\cdot}0442\beta$) is thus substantiated. The lowest aromatic stabilization ($\mathrm{REPE} < 0{\cdot}030\beta$) was found in the isomeric naphthoquinone methides *Va*, *VIa*, *VIIa*, *IX* and *X*. These systems can be regarded as non-aromatic cross-conjugated enones. Compound *VIIa* has the lowest REPE value of the whole series ($0{\cdot}0255\beta$); this illustrates well the increased instability of polycyclic molecules forced to exist in a completely developed quinonoid structure. Similar conclusions have been published also for the corresponding hydrocarbons[16] and quinones[28].



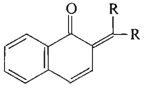
Ia; R = H
Ib; R = C_6H_5



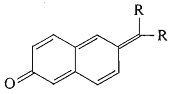
IIa: R = H
IIb; R = C_6H_5



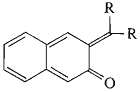
IIIa; R = H
IIIb; R = C_6H_5



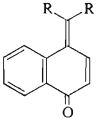
IVa; R = H
IVb; R = C_6H_5



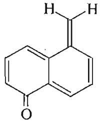
Va; R = H
Vb; R = C_6H_5



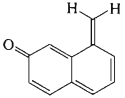
VIa; R = H
VIb; R = C_6H_5



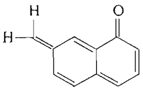
VIIa; R = H
VIIb; R = C_6H_5



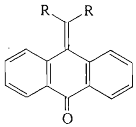
VIII



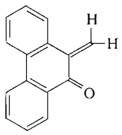
IX



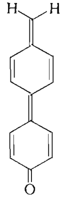
X



XIa: R = H
XIb: R = C_6H_5

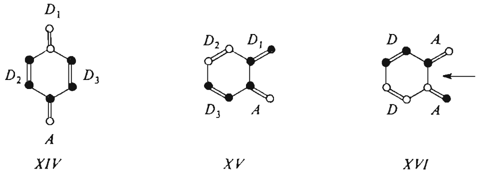


XII



XIII

It is interesting to compare the results of HMO calculations of resonance energies with qualitative results of the graph theory[30,31]. According to this theory, the degree of cyclic electron delocalization in the parent quinone methides *Ia* and *IIa* is a function of both the donor–acceptor arrangement of the components and conservation of orbital phase continuity. In this respect, the parent quinone methides correspond to the conjugation modes *XIV* and *XV* (Scheme 1) which in both cases can be described as continuous cyclic conjugation with electron delocalization.



SCHEME 1

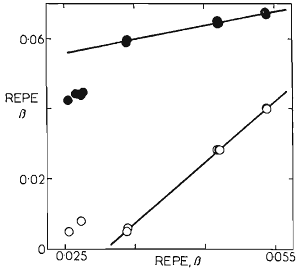


FIG. 1

Graphical Representation of the Linear Relations ($REPE_Q$) = f($REPE_{QM}$) (●) and ($REPE_{QDM}$) = f($REPE_{QM}$) (○)

Strictly speaking, we can use this model only for evaluation of the parent quinone methides and their substituted derivatives since the theory does not involve a description of *ortho*-condensed systems. In an approximation, annelation also can be formally regarded upon as a substitution indicating the change of electron donor ability D_2 and D_3 of the double bonds. The annelated nucleus behaves like a formal electron donor (compare *e.g.* half-wave potential of *p*-benzoquinone (−0·51 V) with that of 1,4-naphthoquinone (−0·71 V) and due to higher electron donor ability D_2 and D_3 the weight of the modes *XIV* or *XV* increases. In case of the presence of phenyl groups on the methide carbon atoms, the decisive factor is rotation of the phenyl groups: it gives rise to either acceptor or donor character of the $C=C(C_6H_5)_2$ fragment. Whereas in the *para* series the donor character still may be retained, in the *ortho* series there is a significant increase in contribution of the mode *XVI* (acceptor character), which represents a type of conjugation with out-of-phase orbitals (the arrow indicates the point at which the orbital phase continuity is interrupted). This fact is manifested by greater tendency of *o*-benzhydrylidene derivatives to electron localization (non-aromaticity) as compared with the *para* series. Thus, it seems that, qualitatively, both these independent criteria of aromatic stabilization of quinone methides afford the same results.

It is noticeable that in the studied quinone methides aromatic stabilization, expressed by REPE values, does not parallel stability in the common laboratory sense. This discrepancy is greatest in the case of phenanthrenequinone methide *XII* (REPE = 0·0539β) which, in spite of its high REPE value (about 70% of the value for benzene after normalization to $\text{REPE}_{\text{benzene}}$ = 1·000β) has not as yet been isolated, although other quinone methides with comparable REPE values are known in the crystalline state (*e.g. Ib*; REPE = 0·0442β; *IIIb*, REPE = 0·0480β or *XI*, REPE = = 0·0539β). Similar situation exists in the case of 1,2- and 2,1-naphthofuchsones (REPE = 0·0414β and 0·0410β, respectively) whose unsubstituted analogues *IIIa* (REPE = 0·0470β) and *IVa* (REPE = 0·0472β) have also not been isolated. These discrepancies can be explained in two ways: either *1*) aromatic stabilization does not parallel the quinone methide reactivity, or *2*) the HMO model is not suitable for description of the complex quinone methide system. Concerning the second case, it is important whether the unified topological HMO approach is capable of describing the alteration of bonds in quinone methides. We therefore compared the bond lengths, calculated from the bond order according to the recommended procedure[32], with those in *Ia*, *IIa* and *IIIa*, determined either experimentally[24] or by complete optimization of the molecular geometry[33,34]. As seen from Table III, the agreement is quite satisfactory. We thus assume that the discrepancy between the calculated aromatic stability and stability in the experimental sense is caused rather by the first alternative.

Since in general the reactivity of the exocyclic carbon $C_{(7)}$ along the pathway (*A*) depends, according to HSAB theory, on substituents and hardness of the attacking reagent, we calculated reactivity indices by the Klopman procedure within the range of single orbital reagent energies (+0·3β to −0·1β). According to perturbation theory, the covalent interaction between two centers is described by the general expression (*1*)

$$E_{ij} = 2\sum_{m}^{occ}\sum_{n}^{unocc}\frac{(c_{im}c_{jn}H_{ij})^2}{\varepsilon_n - \varepsilon_m} + 2\sum_{m}^{unocc}\sum_{n}^{occ}\frac{(c_{im}c_{jn}H_{ij})^2}{\varepsilon_m - \varepsilon_n}, \quad (1)$$

where c_i and c_j are expansion coefficients of the reacting centers, ε_n and ε_m are energies of the occupied and unoccupied orbitals and H_{ij} is the resonance integral between the atomic orbitals. Only the first term is significant in the case of an attack by a nucleophile. Since from the experimental point of view the isolability of a quinone methide depends on its reaction with water, *i.e.* hard nucleophile, we took as a criterion the index, corresponding to $\varepsilon_n = +0{\cdot}3\beta$. The resonance integral H_{ij} was assumed to be constant. Further simplification, $c_{jn} = 1$, follows from the approximation of the single-orbital reagent. Concerning reactivity of quinone methides, the equations (*B*) and (*C*) are also important.

TABLE III

Bond Lengths (r_{ij}, nm) in Quinone Methides *Ia*, *IIa* and *IIIa*

Bond[a]	*I*		*IIa*		*IIIa*	
	HMO[b]	ref.[33]	HMO[b]	ref.[34]	HMO[b]	ref.[24]
C1—O	0·1236	0·121	0·1232	0·123	0·1233	0·1221
C1—C2	0·1440	0·1500	0·1438	0·1495	0·1443	0·1458
C2—C3	0·1350	0·1350	0·1361	0·1355	0·1353	0·1330
C3—C4	0·1445	0·1491	0·1423	0·1459	0·1440	0·1445
C4—C5	—	—	0·1361	0·1357	0·1421	0·1407
C5—C6	—	—	0·1439	0·1474	0·1449	0·1483
C4—C7	0·1366	0·1344	—	—	—	—
C6—C7	—	—	0·1361	0·1359	0·1385	0·1359
C1—C6	—	—	0·1462	0·1513	0·1454	0·1502
C3—C5	—	—	—	—	0·1406	0·1401
C'3—C'4	—	—	—	—	0·1384	0·1377
C'4—C'5	—	—	—	—	0·1397	0·1379
C'5—C'6	—	—	—	—	0·1383	0·1373
C'6—C4	—	—	—	—	0·1408	0·1395

[a] Substituents on methide carbon atom are not considered; [b] calculated according to ref.[32].

Using simple rules, derived from the theory of frontier orbitals, we can evaluate the ease of cyclodimerization reaction from the difference between the HOMO and LUMO energies of the substrates. This approach has been successfully applied to the determination of stability criteria in the quinone series[35]. In this study a more sophisticated procedure has been used. According to the equation (*1*), the σ bond will be formed between such two centers which afford the highest ΔE_{ij} value, *i.e.* the maximum overlap stabilization. Since in all quinone methides the most significant interaction is that between the methide carbon atoms, we can in this way compare the reactions (*B*) and (*C*).* The numerical values of the reactivity indices ΔE_i and ΔE_{ij} are summarized in Table IV.

If we compare the values in Table IV with the actual stability of quinone methides, it seems that the critical value of ΔE_{ij} is about $0{\cdot}34\beta^{-1}$, All the hitherto isolated quinone methides (*Ib*, *IIIb*, *IVb*, *VIIb*, *XIa* and *XIb*) have the calculated ΔE_{ij} equal or smaller than $0{\cdot}334\beta^{-1}$. The whole studied series contains two compounds with ΔE_{ij} smaller than the mentioned critical value which have not been as yet isolated: 2,6-naphthofuchsone (*Vb*, $\Delta E_{ij} = 0{\cdot}319\beta^{-1}$) and 2,3-naphthofuchsone (*VIb*, $\Delta E_{ij} = 0{\cdot}326\beta^{-1}$).

TABLE IV

Chemical Reactivity Indices of Quinone Methides *I*—*XIII*

Compound	$\Delta E_i[\beta^{-1}]^a$	$\Delta E_{ij}[\beta^{-1}]^b$	Compound	$\Delta E_i[\beta^{-1}]^a$	$\Delta E_{ij}[\beta^{-1}]^b$
Ia	1·6139	0·471	*VIb*	1·4998	0·326
Ib	1·2240	0·275	*VIIa*	1·3772	0·423
IIa	1·5847	0·451	*VIIb*	1·0643	0·259
IIb	1·2670	0·292	*VIII*	1·8897	0·590
IIIa	1·3277	0·387	*IX*	1·8806	0·543
IIIb	1·0853	0·264	*X*	1·9819	0·633
IVa	1·3868	0·421	*XIa*	1·1758	0·334
IVb	1·1182	0·280	*XIb*	0·9220	0·242
Va	1·9846	0·595	*XII*	1·2410	0·376
Vb	1·4574	0·319	*XIII*	2·2465	0·665
VIa	1·9117	0·526			

[a] For evaluation of Klopmans reactivity index reagent energy level $+0{\cdot}3\beta$ was used; [b] for definition see Eq. (*1*).

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* It must be mentioned that in quinone methides substituted on $C_{(7)}$ also other types of interactions should be considered (*e.g.* those between the exocyclic carbon and the carbonyl oxygen — "head-tail" type). Since the aim of this study was not to investigate the regioselectivity of dimerization reactions, we shall not treat probability of the particular interaction types.

The higher index for 9,10-phenanthrenequinone methide (XII; $\Delta E_{ij} = 0{\cdot}376\beta^{-1}$) than for 9,10-methyleneanthrone (XI; $\Delta E_{ij} = 0{\cdot}334\beta^{-1}$) is also worth notice: it indicies that the lower stability of the phenanthrene derivative XII could be caused by its tendency to dimerize. Evaluation of the overall stability of quinone methides must necessarily be based on all the three partial criteria and take into account the resonance energies per electron (REPE) as well as the perturbation indices (ΔE_i) and interaction energies between the exocyclic carbon atoms (ΔE_{ij}). Graphical solution of the function $p = f(1/\text{REPE}, \Delta E_i, \Delta E_{ij})$ in the coordinates x, y, z together with the experimental experience, allows us to estimate also the integration limits for description of the space corresponding to "stable" quinone

TABLE V

Comparison of Predicted and Experimental Stabilities of Quinone Methides *I*—*XIII*

Compounds	P^a	Stability[b]	Reference[c]
XIb	100·0	stable	37, 4
VIIb	76·2	stable	38
IIIb	67·7	stable	24, 39
XIa	60·0	stable	8, 40
IVb	57·8	stable	39
Ib	57·4	stable	7, 40
XII	50·5	moderately stable	41
IIb	42·1	moderately stable	this work
IIIa	40·2	moderately stable	18
Vb	37·2	moderately stable	this work
VIIa	35·3	—	—
IVa	35·2	—	—
VIb	29·4	moderately stable	this work
IIa	20·7	unstable	5
Ia	19·6	unstable	6
VIa	11·9	unstable	this work
IX	11·6	—	—
VIII	10·9	—	—
Va	9·4	—	—
X	9·3	—	—
XIII	8·9	—	—

[a] For definition see equation (*2*); [b] the term stability is used in the everyday laboratory sense, *i.e.* stable denotes isolable compounds with well defined properties, moderately stable denotes compounds stable in solution or when isolated, with a limited lifetime, unstable denotes reactive, transient and short lived species; [c] reference to the preparative work.

methides: this is defined by the expression

$$\int_0^{24.4}\int_0^{1.22}\int_0^{0.34} \mathrm{d}(1/\mathrm{REPE})\,\mathrm{d}(\Delta E_i)\,\mathrm{d}(\Delta E_{ij})\,.$$

The aromatic stabilization and reactivity index values of all the studied quinone methides indicate that particularly compounds *IIb*, *Vb*, *VIb* and *XII* might be isolated. Their REPE values (0·0356β, 0·0395β, 0·0329β and 0·0539β, respectively) are comparable with that of the stable cyclopropenone (REPE = 0·0340β) and also their reactivity indices are not extremely high. Although in our preparative experiments we thoroughly excluded moisture and air oxygen, we were not able to isolate the above-mentioned quinone methides in the crystalline form. A typical representative of "less stable" quinone methides is 2,3-naphthoquinone methide (*VIa*, REPE = 0·0274β, $\Delta E_{ij} = 0{\cdot}526\beta^{-1}$ and $\Delta E_i = 1{\cdot}912\beta^{-1}$). With the exception of compound *VIa* for which even the UV measurement was difficult due to its rapid disappearance, the other compounds are relatively stable in solution and their spectra exhibited well defined absorption maxima.

Instead of considering each of the stability factors separately, we can combine their suitably chosen set into one stability index, although it is naturally difficult to estimate the relative significance of the factors chosen[36]. If we consider anthrafuchsone (*XIb*) as an "ideally" stable quinone methide, the "stability" index P for quinone methides can be defined by equation (*2*) where 437·4 is the normalization constant.

$$P = 437{\cdot}4\,\frac{\mathrm{REPE}}{\Delta E_i\,.\,\Delta E_{ij}} \tag{2}$$

The stability indices of quinone methides *XIb*, *VIIb*, *IIIb*, *XIa*, *IVb* and *Ib* (Table V) are greater than 55·0. All these compounds were isolated in the crystalline form and the value of $P = 55{\cdot}0$ can therefore be regarded as a critical value for the stability of quinone methides. Compounds with the index P lower than the mentioned values have not as yet been prepared in the crystalline state, however, it is obvious that also for this group of quinone methides the P indices express well the experimental experience. Whereas great majority of compounds with $30{\cdot}0 < P < 55{\cdot}0$ is stable in dilute solutions in inert solvents, spectral measurements on compounds with $P < 30{\cdot}0$ encounter already substantial experimental difficulties.

We can thus summarize that HMO resonance energies apparently give a real picture of the aromatic stabilization in quinone methides but they do not reflect well their overall stability, taken as a combination of the thermodynamic and kinetic component.

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